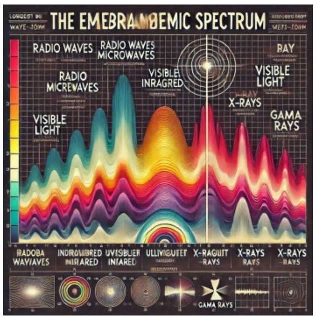
Chapter 1:
Introduction to Spectral Methods



1. Introduction

Spectroscopy is the analysis of electromagnetic radiation emitted, absorbed or diffused by matter (molecules, atoms, etc.). Spectrometry is based on the qualitative and quantitative study of spectra produced by radiation-matter interaction or by matter-matter interaction **.**

2. Matter - radiation interaction :

2.1 Radiation :

Wave nature : Electromagnetic radiation (or electromagnetic radiation) is a wave made up of two oscillating fields: an electric field E and a magnetic field H, both perpendicular to each other and perpendicular to the direction of propagation.

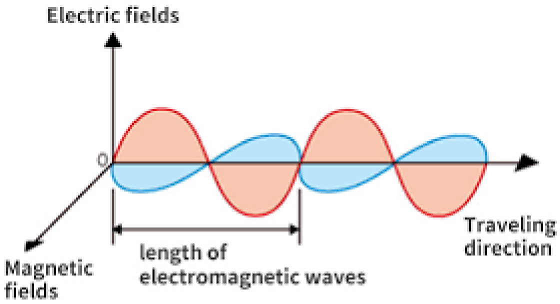


Fig.1: Oscillating fields:

Electric field E/ Magnetic field H

Electromagnetic radiation is characterized by its frequency, wavelength or wave number.

Frequency (Hertz)	Wavelength (m)	Wave number (m^{-1})
$\nu = \frac{1}{T}$	$\lambda = cT = \frac{c}{\nu}$	$\bar{\nu} = \frac{1}{\lambda}$

- *T: period (Second)*
- *c = speed of light (= 3.10* ^{8} *ms* $^{-1}$*)*

The energy of radiation is related to the previous quantities by the fundamental Planck relation:

$$E = h\nu$$

- *h is **Planck's constant** . It is equal to 6,624.10 $^{-34}$ Js*

All radiation constitutes the electromagnetic spectrum.

2.2 Electromagnetic spectrum:

The electromagnetic spectrum represents the set of electromagnetic waves classified according to their wavelengths (λ: lambda) or their frequencies (ν: nu). Each region of the spectrum is associated with specific interactions with matter.

The spectrum is divided into several regions:

a) Radio Waves
b) Micro-Waves
c) Infrared
d) Visible Light
e) Ultraviolet
f) X-rays
g) Gamma rays

2.3 Characteristics of Electromagnetic Waves

Electromagnetic waves are defined by:

- **Wavelength (λ)** : Distance between two consecutive peaks
- **Frequency (ν)** : Number of oscillations per second.
- **Energy (E)** : Related to frequency by Planck's relationship:

Table 1: Characteristics of electromagnetic waves

Wave type	Wavelengths (m)	Frequency (Hz)	Energy (eV)
Gamma rays	< 0.01 nm	$> 3 \times 10^{19}$	$> 10^{5}$
X-rays	0.01 - 10 nm	$3 \times 10^{16} – 3 \times 10^{19}$	$124 - 10^{6}$
Ultraviolet (UV)	10 – 400 nm	$7.5 \times 10^{14} – 3 \times 10^{16}$	3.1 - 124
Visible light	400 – 700 nm	$4 \times 10^{14} – 7.5 \times 10^{14}$	1.7 – 3.1
Infrared (IR)	700 nm – 1 mm	$3 \times 10^{11} - 4 \times 10^{14}$	$10^{3} – 1.7$
Micro - wave	1mm – 1m	$3 \times 10^{8} - 3 \times 10^{11}$	$10^{6} – 10^{3}$
Radio - waves	> 1	$< 3 \times 10^{8}$	$< 10^{6}$

2.4 Corpuscular nature :

The wave nature of light alone does not allow us to interpret the phenomena of interaction between light and matter. **Planck** and then **Einstein** proposed quantum theory:

Light is composed of grains of energy: photons. The photon is a particle that propagates at the speed of light and has a quantum of energy: $E = h\nu$; h is Planck's constant.

3. Molecular energy levels :

An elementary particle (atom, ion or molecule) can only exist in certain quantized energy states. In the case of a molecule, the total energy is considered to be the sum of the terms:

E_t (total) = E_e (electronic) + E_v (vibrational) + E_r (rotational) + E_s (spin) + E_T (translational)

The orders of magnitude are very different:

$$\mathbf{E_e > E_v > E_r > E_s > E_T}$$

(a) Electronic State: The electronic state corresponds to the arrangement of electrons in molecular orbitals. Each molecule has several electronic states, but it is generally stable in its ground state.

(b) Vibrational State: The vibrational state is associated with the periodic oscillations of atoms within a molecule. These vibrations affect **bond lengths** and **bond angles** .

- **Stretching vibrations** → The bond lengthens and contracts.
- **Bending vibrations** → Bond angles change.

(c) Rotational State: The rotational state is associated with the rotation of the molecule around its axes of inertia. Only **asymmetric molecules** can possess a rotational spectrum.

(d) **Spin State:** The **spin state** is a quantum state associated with the **intrinsic angular momentum** of a particle, such as an electron, proton, or atomic nucleus.

3.1 Note:

- Electronic transitions are the most energetic (UV-Visible).
- Molecular vibrations are less energetic (IR).
- Molecular rotations are even weaker (Microwaves).
- Spin energy is negligible except in the presence of a magnetic field.
- A **photon is a massless** elementary particle that carries a **discrete amount of electromagnetic energy** .

3.2 Characteristics of the photon:

- Moves at the **speed of light $c=3.00\times10^8$ m/s** .
- Has an **energy E=hν** Carrier of **electromagnetic interaction** .
- Can be absorbed or emitted during a quantum transition in an atom or molecule.

Example :

- A UV photon can excite an electron in a molecule.
- An infrared photon can induce a molecular vibration.
- A microwave photon can cause a rotational transition.

3.3 Energy diagram

The electronic, vibrational and rotational energy levels are represented by a diagram in which each level is represented by a horizontal line and characterized by a set of quantum numbers n, v and J linked respectively to the electronic, vibrational and rotational movements of the molecule.

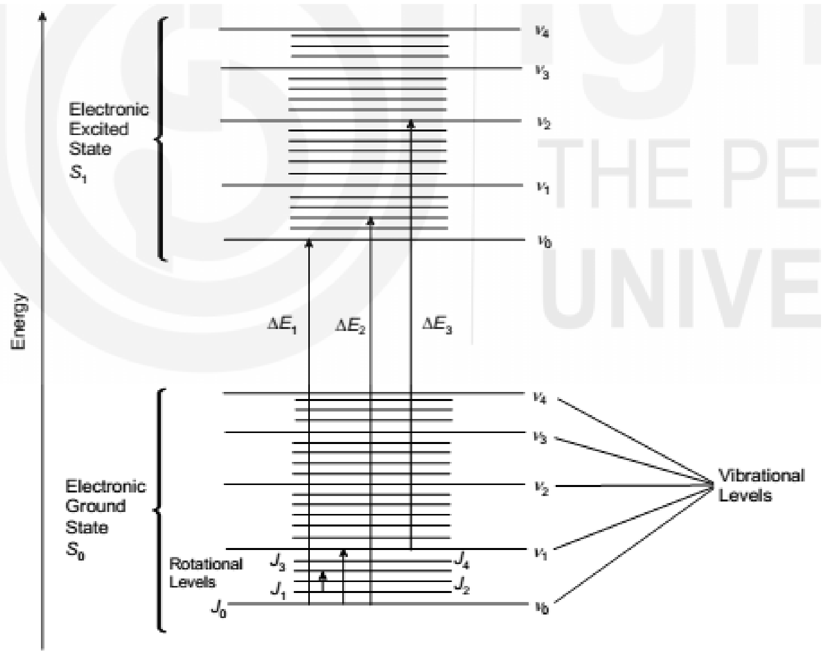


Fig. 2: Energy diagram

Each elementary particle (atom, ion, or molecule) has a unique set of energy states. The particle can be in any of these states. The number of particles on a given energy level is called the **population** . The population on a level i relative to the population of the fundamental level obeys **the Maxwell-Boltzmann distribution law** :

$$\frac{N_i}{N_0} = \frac{g_i}{g_0} e^{-\left[\frac{E_i - E_0}{kT}\right]}$$

- **N_i :** number of particles in excited state i
- **N_0 :** number of particles in the ground state 0
- **g_i and g_0** : degeneracy of states i and 0 respectively
- **E_i and E_0** : energy of states i and 0 respectively?
- **k:** Boltzmann constant ($1.38.10^{-23}$ JK^{-1})
- **T:** temperature in Kelvin. Using this relationship, we show that at room temperature:

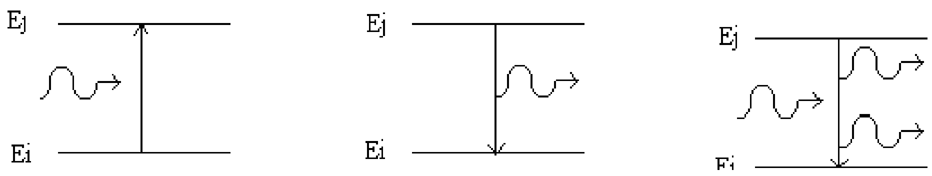
4. Interaction between wave and matter

Energy exchanges between matter and radiation can only take place by quanta: **ΔE =h** ν. Four processes are at the basis of spectroscopic phenomena: *absorption, spontaneous emission, stimulated emission (case of lasers) and diffusion* .

a. absorption,

b. spontaneous emission

c. stimulated emission (case of lasers)
d. diffusion .



Absorption Spontaneous emission Stimulated emission

a. Absorption :Absorption is a phenomenon where an atom, molecule, or material captures **the energy of a photon** and converts it into another form of internal energy (electronic, vibrational, or thermal).

b. Spontaneous Emission: Spontaneous emission is the process by which an electron **spontaneously returns** to a lower energy state, releasing a photon of frequency ν.

c. Stimulated Emission (Case of Lasers) :Stimulated emission is the process where an incident photon of frequency ν **forces** an excited electron to return to a lower state, **emitting a photon identical** in phase and direction.

d. Scattering : Scattering is a phenomenon where a photon **changes direction** when interacting with a particle or medium, without being absorbed or emitted.

Table 2: Spectroscopic phenomena

Phenomenon	Definition	Example
Absorption	An atom or molecule absorbs a photon and enters an excited state.	UV-Vis spectroscopy, tinted sunglasses.
Spontaneous emission	An excited atom returns to its ground state and emits a photon randomly.	LED, fluorescence.
Stimulated emission	An incident photon triggers the emission of another identical photon.	Lasers.
Diffusion	A photon changes direction without being absorbed or re-emitted.	Blue sky (Rayleigh), Raman spectroscopy.

4.1 The Different Types of Absorption

The absorption of light or an electromagnetic wave by a medium can be classified into several categories depending on the nature of the absorbing system (molecules, atoms, solids, etc.).

- Molecular Absorption : Molecular absorption is due to electronic, vibrational, and rotational transitions in a molecule.

- Atomic Absorption: Atomic absorption concerns the transitions between the energy levels of electrons in an atom.

- Absorption in Solids (Condensed States) : Absorption in solids is due to electronic transitions in the crystal structure or interactions with lattice vibrations (phonons).

- Raman Absorption: Raman absorption is a process where an incident photon is inelastically scattered, causing a frequency change corresponding to a vibrational transition.

- Resonant Absorption (Resonance Effect - Fluorescence): When a system absorbs an electromagnetic wave at a frequency exactly matching its resonance frequency, the absorption is maximized.

- X-ray and Gamma Absorption (Photoelectric Effect & Compton Effect) : At very high energies, absorption of X-rays and gamma rays occurs by photoelectric effect, Compton scattering and pair production.

5. Definition of Spectral Methods

Spectral methods involve analyzing the interactions between matter and a form of electromagnetic energy. These techniques provide qualitative and quantitative information about the chemical structure, composition, and properties of molecules or materials.

5.1 Fundamental Principle :

When a substance is exposed to electromagnetic radiation, it can absorb, emit, or scatter energy. These phenomena produce characteristic spectra that reflect the nature and properties of the components in the sample.

5.2 Applications :

Spectral methods are used in analytical chemistry, biology, pharmacy, physics, and materials science.

5.3 Types of spectroscopy

There are two main categories:

- Mass spectrometry (which uses matter-matter interaction);
- Radiative spectroscopies (which use radiation-matter interaction).

Depending on the nature of the radiation-matter interaction, two types of radiative spectroscopy are distinguished:

- The received electromagnetic radiation is diffracted. This is X-ray diffraction crystallography. This method allows structural analysis in the solid state (crystallized matter).
- The received electromagnetic radiation is absorbed by matter. Depending on the wavelength of the radiation and the extent of absorption, we distinguish:
  - Molecular spectroscopy: UV-Vis, atomic absorption and infrared;
  - NMR (nuclear magnetic resonance) spectroscopy which allows hydrogens to be located (thanks to their nuclear spin magnetic moment), i.e. the structure of the carbon skeleton.

Spectroscopy is an analytical technique that studies the interaction between matter and a form of electromagnetic radiation. It is classified into different types depending on the nature of the interaction and the information obtained.

(a)Absorption spectroscopy

- **Principle:** This method is based on the absorption of energy by a sample, causing electronic, vibrational or rotational transitions. The amount of light absorbed is measured as a function of the wavelength.

- **Examples:**
  - **UV-Visible Spectroscopy:** Studies electronic transitions in chromophores. Used for the quantitative and qualitative analysis of compounds.
  - **Infrared (IR) spectroscopy:** Studies molecular vibrations. Useful for identifying functional groups in organic compounds.
  - **Atomic Absorption Spectroscopy (AAS):** Analyzes electronic transitions in single atoms to detect specific elements.

(b) Emission spectroscopy

- **Principle:** After excitation, atoms or molecules release energy in the form of radiation. The emitted light is analyzed to identify and quantify the elements.
- **Examples:**
  - **Atomic emission spectroscopy:** Studies the emissions of excited atoms, often used in inductively coupled plasma (ICP-AES).
  - **Fluorescence spectrometry:** Uses the emission of light from excited molecules. Very sensitive for specific compounds.

(c) Resonance spectroscopy

- **Principle:** This method is based on transitions between energy states in an external field, such as a magnetic field.
- **Examples:**
  - **Nuclear magnetic resonance (NMR) spectroscopy:** Studies the interactions between nuclear spins and a magnetic field. Used to determine molecular structure.
  - **Electron spin resonance (ESR) spectroscopy:** Studies species containing unpaired electrons, such as free radicals.

(d) Scattering spectroscopy

- **Principle:** Based on the scattering of light by a molecule or particle, without significant absorption.
- **Example :**
  - **Raman spectroscopy:** Analyzes frequency changes in scattered light to identify molecular vibrations.

(e) Mass spectroscopy

- **Principle:** The molecules are ionized, fragmented, then sorted according to their mass/charge ratio (m/zm).
- **Applications:** Identification of organic compounds, determination of molar masses and isotopic analyses.

(f) X-ray spectroscopy

- **Principle:** X-ray absorption or diffraction is used to analyze the atomic and crystalline structure of materials.
- **Examples:**
  - **X-ray fluorescence spectroscopy (XRF):** Detection of chemical elements.

- **X-ray diffraction (XRD):** Analysis of crystal structures.

(g)Electron spectroscopy

- **Principle:** Studies electrons ejected from a material under the effect of radiation or interaction.
- **Examples:**
    - **Photoelectron spectroscopy (XPS):** Analysis of chemical bonds and electronic states.
    - **Auger spectroscopy:** Study of surfaces and thin films.

(h) (Vibrational spectroscopy

- **Infrared (IR):** Detects molecular vibrations.
- **Raman:** Complementary to IR, detects asymmetric vibrations.

(i) Laser spectroscopy

- **Principle:** Use of a laser as a light source to excite the sample.
- **Applications:** Sensitive detection, environmental analysis and biological imaging.

(j) Fluorescence spectroscopy

- **Principle:** Analysis of photons emitted by a material following light excitation.
- **Applications:** Molecular biology, fluorescent labeling.

6. Types of spectra

- Continuous spectra: All radiation is observed without discontinuity. These spectra are characteristic of light emitted by very hot bodies (the sun, an incandescent lamp). The graph opposite represents the spectral distribution of light emitted by a tungsten lamp heated to 300 K.

- Line spectra: Consisting of a series of narrow, well-defined peaks related to the excitation of individual atoms. These spectra are characteristic of monatomic gases, under low pressure, subjected to an electrical discharge (mercury vapor lamp).

- Band spectra: Consisting of several groups of lines so close that they cannot be completely resolved. They are due to small molecules or radicals.